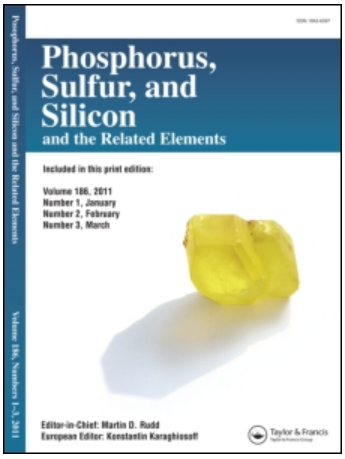

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Synthesis of Some New 3-Alkylthio Derivatives of 1-Phenyl-1H-[1,3,4]thiadiazino[5,6-b]quinoxalines

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*The synthesis of some new 3-(alkylthio)-1-phenyl-1H-[1,3,4]thiadiazino[5,6-b]quinoxalines **4** have been achieved by cyclocondensation reaction of the alkyl-2-phenylhydrazinecarbodithioates **1** with 2,3-dichloroquinoxaline **2** in basic N,N-dimethylformamide.*

Keywords 2,3-Dichloroquinoxalies; 2-phenylhydrazinecarbodithioate; cyclocondensation; thiadiazinoquinoxalines

Several derivatives of [1,3,4]thiadiazino[5,6-b]quinoxaline ring system are known. Few routes have been developed for the synthesis of such derivatives, which include the ring expansion of 3-amino-2-iminothiazolo[4,5-b]quinoxaline[1] and the cyclization of N-alkylazinium cations or 2,3-dichloroquinoxaline with bifunctional nuclephiles such as thiohydrazides and dithizone.[2–4] We decided to use the latter approach for the preparation of previously undescribed (to our knowledge) 3-alkylthio-1-phenyl-[1,3,4]thiadiazino[5,6-b]quinoxalines **3**.

Our approach is based on the cyclocondesation reaction of 2,3-dichloroquinoxaline **2** with alkyl-2-phenylhydrazinecarbodithioate **1** in basic N,N-dimethylformamide. As shown in Scheme 1, the starting alkyl-2-phenylhydrazinecarbodithioates **1** which were prepared according to Ried[5] underwent heterocyclization with 2,3-dichloroquinoxaline **2** in boiling N,N-dimethylformamide in the presence of sodium carbonate to afford the 3-alkylthio derivatives of 1-phenyl-1H-[1,3,4] thiadiazino[5,6-b]quinoxaline **3**. The structures assigned to compound **3** was substantiated by their spectral data (Table I). The ^{1}HNMR spectra of

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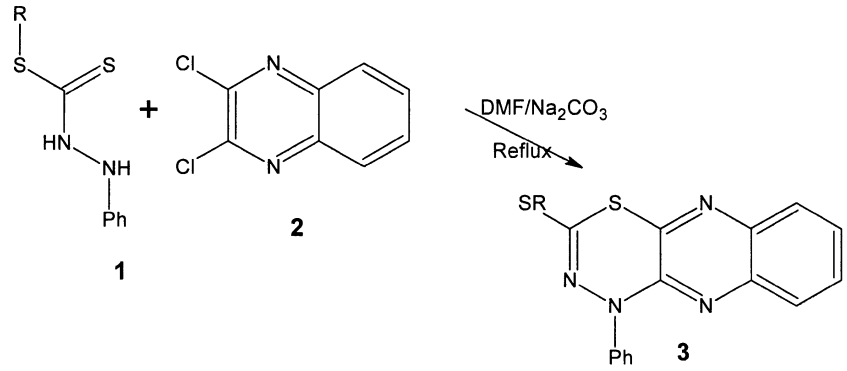
TABLE I Physical and Spectral Data of 3-(Alkylthio)-1-phenyl-1H-[1,3,4]thiadiazino[5,6-b]quinoxalines 3 a–f

Entry	Yield (%)	M.P (°C)	Spectral data	Molecular formula	C% [calc]	H% [calc]	N% [calc]	S% [calc]
3a	30	168–171	^{1}HNMR: ($CDCl_3$) δ, 2.54 (s, 3H, CH_3), 7.2–7.9 (multiplet, 9H) IR (KBr disk): ν, 750 cm^{-1}, 1000 cm^{-1}, 1400 cm^{-1}, m/z, 324, 326, 323, 325, 277	$C_{16}H_{12}N_4S_2$	59.53 [59.23]	3.71 [3.73]	17.24 [17.27]	19.52 [19.77]
3b	25	290–291 (dec)	^{1}HNMR: ($CDCl_3$) δ, 1.4(t, 3H,CH_3), 3.1(q, 2H, CH_2), 7.2–7.9 (multiplet, 9H) IR (KBr disk): ν, 750 cm^{-1}, 1000 cm^{-1}, 1250 cm^{-1}, 1400 cm^{-1}, m/z, 338, 340, 337, 339, 277	$C_{17}H_{14}N_4S_2$	60.25 [60.33]	4.19 [4.17]	16.59 [16.55]	18.90 [18.95]
3c	30	98–100	^{1}HNMR: ($CDCl_3$) δ, 1(t, 3H,CH_3), 1.7(sextet, 2H, CH_2), 3.06(t, 2H, S-CH_2) 7.2–7.9 (multiplet, 9H) IR (KBr disk): ν, 750 cm^{-1}, 1000 cm^{-1}, 1250 cm^{-1}, 1400, cm^{-1}, m/z, 352, 354, 351, 353, 277	$C_{18}H_{16}N_4S_2$	61.15 [61.33]	4.55 [4.58]	16.05 [15.90]	18.23 [18.19]
3d	25	94–96	^{1}HNMR: ($CDCl_3$) δ, 0.91(t, 3H, (CH_3)-CH_2), 1.4 (d, 2H, (CH_3)-CH), 1.7(dq, 2H,CH_2) 7.2–7.9 (multiplet, 9H) IR (KBr disk): ν, 750 cm^{-1}, 1000 cm^{-1}, 1250 cm^{-1}, 1400 cm^{-1}, m/z, 366, 368, 365, 367, 277	$C_{19}H_{18}N_4S_2$	62.40 [62.26]	4.85 [4.95]	15.40 [15.29]	17.3 [17.5]
3e	28	146–148	^{1}HNMR: ($CDCl_3$) δ, 0.91(t, 3H,CH_3), 1.3–1.8(multiplet, 4H, $2CH_2$), 3.1(t, 2H,S-CH_2) 7.2–7.9 (multiplet, 9H) IR (KBr disk): ν, 750 cm^{-1}, 1000 cm^{-1}, 1250 cm^{-1} 1400 cm^{-1}, m/z, 366, 368, 365, 367, 277	$C_{19}H_{18}N_4S_2$	62.35 [62.26]	4.88 [4.95]	15.41 [15.29]	17.32 [17.5]
3f	27	132–135	^{1}HNMR: ($CDCl_3$) δ, 4.35(s, 2H, CH_2), 7.2–7.8(multiplet, 14H) IR (KBr disk): ν, 700 cm^{-1}, 750 cm^{-1}, 1000 cm^{-1}, 1250 cm^{-1}, 1400 cm^{-1}, m/z, 400, 402, 399, 401, 277	$C_{22}H_{16}N_4S_2$	66.11 [65.97]	4.01 [4.03]	14.10 [13.99]	15.8 [16.01]

compound **3** was devoid of the signals at δ 6.0 and 9.0 ppm for the NH groups of the precursor **1** and showed further downfield shifts for aromatic protons indicating the construction of a thiadiazine ring around positions 2 and 3 of the quinoxaline ring. Further proof came from their IR spectra, which lacked the N-H stretching frequencies of their precursor **1**. Mass spectra showed the expected molecular ion peak and the fragmentation pattern is in accord with the proposed structure.

In summary, some new 3-(alkylthio)-1-phenyl-1H-[1,3,4]thiadiazino-[5,6-b]quinoxalines have been synthesized by a direct synthetic route and their structures were established by their spectral data.



SCHEME 1 R = a: Me, b: Et, c:n-Pr, d: n-Bu, e: iso-Bu, f: Benzyl.

EXPERIMENTAL

Melting points were recorded on an Electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300 Shimadzu Spectrometer. The ^{1}HNMR (100 MHz) spectra were recorded on Bruker AC 100 Spectrometer. Mass spectra were scanned on a Varian Mat CH-7 at 70 eV. Elemental analysis was performed on a Thermofinnigan Flash EA micro analyzer.

General Procedure for the Preparation of 3-(Alkylthio)-1-phenyl-1H-[1,3,4]thiadiazino[5,6-b]quinoxalines 3a–f

A mixture of 2,3-dichloroquinoxaline **2** (2.5 mmol, 0.5 g), alkyl-2-phenylhydrazinecarbodithioate **1** (2.5-mmol) and sodium carbonate (0.3 g,) in DMF (25 ml) was heated under reflux for 3 h. After the reaction was complete, the mixture was cooled to room temperature and water (100 mL) was added. The mixture was extracted with $CHCl_3$ (3×15 mL) and the combined organic extracts were dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue

was purified by column chromatography over silica gel that was eluted with chloroform:hexane (1:1). The products were obtained as yellow solids. Yields and melting points are listed in Table I.

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